SCIENCE FOR GLASS PRODUCTION

CONDITIONS FOR TRANSFORMATION AND EQUILIBRIUM OF IRON OXIDES IN GLASS MELTING

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It is demonstrated that transformations of iron oxides in glass melting occur mainly in the solid phase. The ratio between the two forms of iron oxides in a glass melt is determined by the melt temperature. Achieving an equilibrium with the gaseous medium requires a long time due to high melt viscosity and low diffusion coefficients. To ensure high service parameters in products, one needs stability of raw material compositions and melting process parameters, including diathermancy of the melt.

Iron oxides play an important role in the production of various glass articles, especially tinted glass containers. This is true both for glass-melting processes and automated molding of articles and for their service parameters. Consequently, one should know and take into account the specifics of transformation of iron oxides in industrial glass melting.

The studies in [1, 2] investigate certain conditions for coexistence of two degrees of oxidation in glass-forming melts and the effect of their ratio on some characteristics of glasses. However, chemical transformation processes and conditions for coexistence of iron oxides in industrial glass-forming melts have virtually not been investigated. This is especially true of the stages of heating and melting batches containing reducing and oxidizing agents.

The present study gives the results of studying transformations of iron oxides in production of industrial glass-forming melts taking into account some data previously obtained by the author [3].

For the purpose of identifying the type of transformation and equilibrium of iron oxides in glass, the kinetics of their transformations was studied in batches and glass melts of industrial container glasses with a different content of iron oxides, up to 1.6%. Iron oxides were introduced via chemically pure hematite Fe_2O_3 and milled charcoal was the reducing agent. In studying the conditions of iron oxide equilibrium, glass melt was exposed in a thin layer at different temperatures.

As a batch with the reducing agent is heated, hematite is partly reduced; the degree of reduction in sintered batch and in glass was determined by means of chemical analysis.

The kinetics of Fe_2O_3 reduction in a batch is presented in Fig. 1. The study of the reduction process at different temperatures demonstrated that reduction duration and extent are determined by emergence of the melt. After that the extent of reduction achieved becomes stabilized, and a further modification of the extent of reduction requires a long time.

The studies of transformation and equilibrium of iron oxides in glasses was carried out as applied to glass melting in tank furnaces. Iron oxides in industrial glass-melting tanks are nonuniformly distributed across the melt depth. As the total content of iron oxides in the bottom layer grows, its content of FeO grows as well.
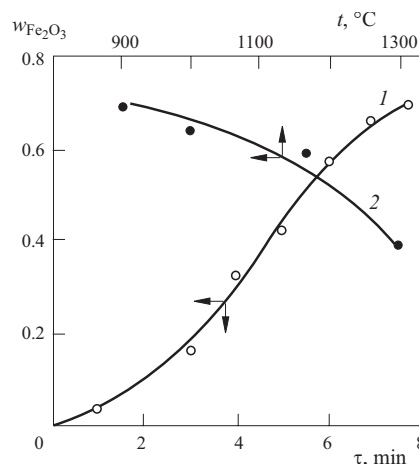
Fig. 1. Variation of the weight fraction of reduced Fe_2O_3 $w_{Fe_2O_3}$ (before melt formation) depending on process duration τ at 900°C (*1*) and on temperature *t* (*2*) with time.

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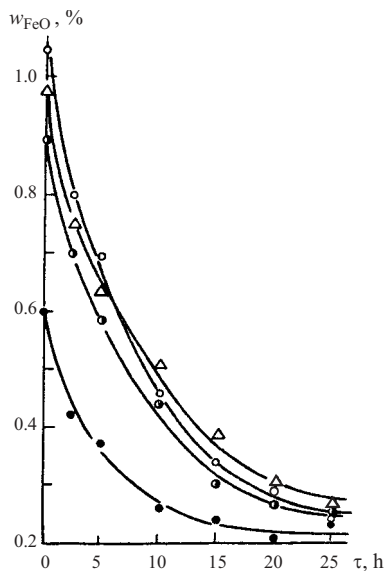
Fig. 2. Kinetics of variation of FeO content w_{FeO} at temperature 1450°C for different initial content.

Fig. 3. Dependence of oxygen diffusion coefficient D on temperature T.

To study the conditions of transformation and equilibrium of iron oxides in a melt, batch sinters and glasses obtained in preceding experiments were milled, melted, and exposed at different temperatures in a relatively thin (0.3 – 0.5 cm) layer in air. Thickness was measured after the end of the experiment.

Experimental results obtained in batch heating (Fig. 1) correspond to reducing conditions. Exposure of the melt in an oxygen-containing atmosphere modifies the ratio between iron oxides. It can be seen in Fig. 2 that attaining an equilibrium ratio of iron oxides in a melt takes time and depends on diffusion of oxygen in the high-viscosity melt. The obtained experimental data can be used to determine the oxygen diffusion coefficient.

This determination is based on a particular case of non-stationary diffusion in a layer with one impermeable bound. For diffusion of oxygen in a melt layer of finite thickness the ratio of the quantity of FeO Q_τ formed within time τ to its initial quantity Q_0 is expressed by the following equation [4]:

$$\frac{Q_\tau}{Q_0} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left[-\theta\,(2m+1)^2\right],$$
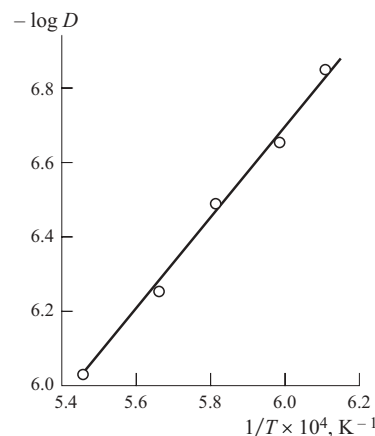
where m is the number of terms in the series; whence

$$\frac{Q_\tau}{Q_0} = 1 - \frac{8}{\pi^2}\left(e^{-\theta} + \frac{1}{9}e^{-9\theta} + \frac{1}{25}e^{-25\theta} + \ldots\right).$$

At the same time

$$\theta = \frac{\pi^2 D \tau}{\delta^2}, \tag{1}$$

where D is the diffusion coefficient and δ is the melt layer thickness.

Sufficient accuracy in calculations can be provided by taking only the first term of the series:

$$\frac{Q_\tau}{Q_0} = 1 - \frac{8}{\pi^2}e^{-\theta}. \tag{2}$$

Formulas (1) and (2) makes it possible to find the diffusion coefficient based on experimental data:

$$D = \frac{\delta^2}{\pi^2 \tau} \ln \frac{8}{\pi^2\left(1 - \dfrac{Q_\tau}{Q_0}\right)}.$$

The diffusion coefficient was calculated as the mean value out of four calculations (Fig. 2). Figure 3 shows the temperature dependence of the calculated diffusion coefficient. The activation energy of the diffusion process in the temperature interval considered is equal to 239.5 kJ/mole.

The mechanism of diffusion transfer of oxygen in glasses is little studied. The authors of several publications assume that oxygen participates in an elementary diffusion action in the form of neutral particles, whereas other authors indicate that oxygen in silicates diffuses in the form of an anion.

The equilibrium between iron oxides in glass melt is expressed as follows:

$$2O^{2-} + 4Fe^{3+} \rightleftarrows 4Fe^{2+} + O_2. \tag{3}$$
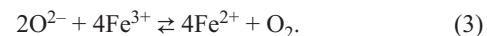
The equilibrium constant in this case is

$$K = \left(\frac{w_{Fe^{2+}}}{w_{Fe^{3+}}}\right)^4 p_{O_2}.$$

For the available experimental data and $p_{O_2} = 0.021$ MPa (air atmosphere), the equilibrium constant at 1450°C is equal to 3.7×10^{-5} MPa. Variations in the equilibrium constant depending on temperature are represented in Fig. 4. The ther-

mal effect of iron oxide transformations found from experimental data is equal to 477.3 kJ.

The studies performed established that the effect of the nature of the gas medium on transformations of iron oxides is mostly manifested at the batch-heating stage. Low diffusion process rates in melts explains why the ratio of iron oxides in industrial glass-melting furnaces, in which glass melt is involved in the production and convective flows, does not correspond to equilibrium conditions.

It was earlier mentioned [5] that FeO has a negative effect on melting and working properties of glasses. This negative effect is intensified as the total content of iron oxides increases. Each glass-melting furnace has an immobile bottom layer of glass melt with a temperature of $1200 – 1300°C$. Oxygen from the gaseous medium of the furnace has virtually no access to that bottom layer due to low diffusion velocities and the presence of migrating production and convective glass-melt flows. Equilibrium (3) in these conditions is shifted to the right. Determination of iron oxide contents in the bottom layers of a number of glass-melting furnaces indicated that the ratio $FeO : Fe_2O_3$ in these furnaces varied within relatively low limits. This shows that despite long-term stay of melted glass in bottom layer, some processes in these layers contribute to maintaining the ratio of iron oxides at a certain constant level. Apparently, as the content of FeO increases, with a shortage of oxygen it can dissociate in accordance with the reversible reaction:

$$3FeO \rightleftarrows Fe + Fe_2O_3.$$

A high content of iron oxides in the bottom layers of glass-melting furnaces and processes occurring in them make these layers perceptibly different from the bulk glass melt in the furnace. Therefore, penetration of such glass into a production flow sharply disturbs the homogeneity of the melt, which, in turn, impairs the service properties of products (mechanical strength, thermal resistance) and causes large-scale breakage and defects. This is especially perceptible under sharp fluctuations in diathermancy of the glass melt. Such fluctuations may arise when the content of iron oxides in initial materials is not constant, or when technological schedules prescribed for a particulate furnace are violated.

Thus, in melting of glasses containing iron oxides, transformations of the latter mainly occur in the solid phase.

The ratio of two forms of iron oxides in a glass melt depends on the melt temperature. Reaching a state of equilib-
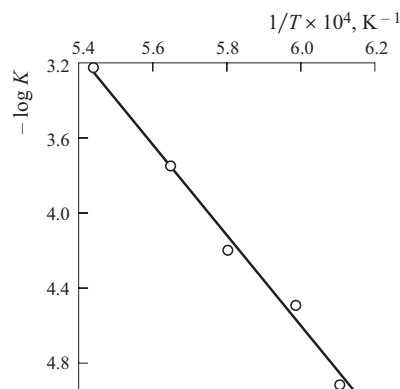

Fig. 4. Temperature dependence of equilibrium constant.

rium with the gaseous medium requires a long time due to high viscosity of the melt and low diffusion coefficients.

The ratio of iron oxides in the bulk glass melt in industrial glass-melting furnaces does not satisfy the condition of equilibrium with the gaseous medium. The equilibrium in the bottom immobile glass melt layers is shifted toward FeO and characterized by a virtually constant level of the $FeO : Fe_2O_3$ ratio.

To decrease the negative effect of FeO on the technological and service parameters of glasses in the automated production of glass articles, it is necessary to use materials with a constant optimum content of iron oxides. This makes it possible to maintain a constant level of diathermancy in the melting tank and stability of technological parameters in glass melting and molding of articles.

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